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(54) Combustible compositions comprising alcohols and fatty acid esters useful in particular as diesel fuels

(57) Combustible compositions, particularly diesel fuels, comprise a stable mixture of from 50 to 90% by volume of at least one C₁₋₈ alkyl ester of a C₁₂₋₂₂ fatty acid, and from 50 to

10% by volume of at least one alcoholic constituent comprising at least one primary, secondary or tertiary aliphatic monohydric C₁₋₅ alcohol. The esters can be obtained by transesterifying certain natural oils and fats; the alcohols by fermentation. The compositions may contain a cetane-number-improving additive, especially if their cetane number does not otherwise exceed 40.

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SPECIFICATION

Combustible compositions comprising alcohols and fatty acid esters useful in particular as diesel fuels

- The present invention concerns novel combustible compositions useful in particular as base fuels for diesel engines. 5
- More particularly the invention concerns compositions which contain at least one alcohol and at least one fatty acid ester as defined in the detailed description of the invention hereinafter.
- It is known that the introduction of alcohols into fuels for diesel engines is a major objective in research for substitute fuels.
- 10 In this respect, experiments have been carried out, for example in Brazil, in regard to operating diesel engines with ethanol to which a fairly high proportion (probably of the order of 10% by weight) of cetane number improving additives is added. 10
- Attempts are also being made to use methanol as a fuel, using non-conventional intake means for supplying the engines, such as for example fumigation or double injection, which are difficult to use and 15 expensive. 15
- Moreover, if the attempt is made to use alcohols mixed with conventional gas oils, a number of serious disadvantages may be encountered.
- First of all, it may happen that the alcohol in question is not miscible with the gas oil; this is the case in particular with hydrated ethanol (for example the water-ethanol azeotrope containing 95% 20 ethanol) or methanol. 20
- The alcohol in question may be miscible with gas oil but the proportion of alcohol to be used is limited by the reduction in the cetane number of the mixture; this is the case with absolute ethanol or n-butanol-acetone mixtures (products of "acetone-butylic" fermentation). A limit may also be imposed by the drop in the viscosity of the mixture, which can give rise to serious problems in regard to wear of the 25 injection system. 25
- It has now been discovered that it is possible to form fuels for diesel engines, containing alcohols, without encountering the above-mentioned disadvantages, provided that said alcohols are associated with certain fatty acid esters. This therefore provides diesel fuels which are free of gas oils and which have both good cetane numbers, suitable viscosity values and, in most cases, satisfactory low- 30 temperature properties. 30
- Such fuels have the characteristic of not containing any substance of petroleum origin.
- Broadly, the fuels according to the invention are defined by a content of from 10 to 50% by volume of at least one substantially alcohol constituent comprising at least one primary, secondary or tertiary aliphatic monohydric alcohol having from 1 to 5 carbon atoms. This may be in particular 35 methanol, absolute ethanol, the ethanol-water azeotrope containing 95% by weight of ethanol, isopropanol, butanols or pentanols, or various mixtures of alcohols primarily containing n-butanol, produced for example by fermentation carried out by means of cellulolytic enzymes on cellulosic substrate hydrolysates. 35
- These fuels also have a content of from 90 to 50% by volume of at least one fatty acid alkyl ester selected from esters in which the acid part derives from a saturated or unsaturated fatty acid containing 40 from 12 to 22 carbon atoms and in which the alkyl part contains from 1 to 8 carbon atoms. 40
- Such fatty acid esters may comprise:
- a) esters of fatty acids, which are unsaturated, with a relatively long chain (from about 16 to 22 carbon atoms),
 - 45 b) esters of fatty acids, which are saturated, with a relatively shorter chain (from about 12 to 14 carbon atoms), and 45
 - c) esters of fatty acids, which are saturated, with a relatively longer chain (from about 16 to 18 carbon atoms).
- The alkyl part of the fatty acid esters considered in the present invention may more particularly 50 comprise methyl, ethyl, isopropyl or 2-ethylhexyl radicals. 50
- The fatty acid esters in accordance with the present invention may derive from natural fatty substances of vegetable or animal origin. In that case, they may advantageously be produced by alcoholysis (or transesterification) by means of a suitable monohydric alcohol, of the glycerol esters contained in the natural fatty substances (oils or greases). The alcoholysis operation may 55 advantageously be carried out on the oils and greases in the crude state, that is to say, without the necessity to separate them into their various glyceridic constituents. This then results in mixtures of fatty acid esters, the composition of the "acid" part of which corresponds to that of the initial fatty substance (oil or grease). 55
- Thus for example, the preparation of alkyl esters derived triglycerides is performed by alcoholysis 60 by means of methanol (for example, under the conditions described in U.S. Patent No. 2 360 844), ethanol, isopropanol or 2-ethylhexanol, according to circumstances. 60
- Examples that may be mentioned of fatty substances of vegetable origin are in particular colza, sunflower, soya, maize, cotton, almond, peanut, olive, palm, palm cabbage, coconut and copra oils. Castor oil (in particular mamona oil) and linseed oil may also be mentioned. However, the latter

two oils suffer from a degree of unsaturation which is much too substantial to produce alkyl esters that can be used as constituents of diesel fuels. In order to be able to use such oils, they will have to be stabilised, by subjecting them to preliminary partial hydrogenation.

5 Examples of fatty substances of animal origin that may be mentioned include in particular lard and tallow. 5

The fatty acid esters used in the present invention may be synthesised, although this is less advantageous, from the fatty acids themselves when such acids are easily available. In that case, operation is by simple esterification of the fatty acid in question by means of the appropriate aliphatic monohydric alcohol (for example methanol, ethanol, isopropanol or 2-ethylhexanol), using any 10 conventional process. 10

The "alcohol constituent" used in the mixtures according to the invention may comprise pure methanol or absolute ethanol, as indicated above. It may also comprise the ethanol-water azeotrope containing 95% by weight of ethanol and 5% by weight of water (it will be referred to hereinafter as "ethanol 95").

15 The alcohol constituent may also be various mixtures containing primarily n-butyl, acetone and/or isopropanol and possibly ethanol. 15

Such mixtures may be for example of the following compositions:

	n-butanol	from 40 to 80% by weight	
	acetone	from 15 to 45% by weight	
20	ethanol	from 0 to 15% by weight	20
	n-butanol	from 45 to 75% by weight	
	isopropanol	from 10 to 40% by weight	
	acetone	from 2 to 15% by weight	
	ethanol	from 0 to 10% by weight	

25 The above-considered compositions can be prepared by simply mixing their various constituents. However, it is also possible for them to be produced in an advantageous manner by a fermentation process which is carried out on a cellulosic substrate hydrolysate, in the presence of at least one cellulolytic enzyme producing microorganism, operating either by acetone/butanol fermentation or by 25 butanol/isopropanol fermentation, to give mixtures of the above-specified compositions.

30 For this purpose, it is possible to use any kinds of cellulosic substrates, for example those produced after pre-treatment of waste paper, cereal straw, bagasse, maize stalks or cobs, lumber or sawmill waste from deciduous and resinous woods. The pre-treatment operation in question may be mechanical (for example crushing) and/or chemical (for example treatment with sodium hydroxide, preferably with about 6% by weight of sodium hydroxide/weight of substrate). 30

35 Sugar hydrolysis (enzymatic reaction) is then performed in accordance with conventional means, preferably at from 30 to 60°C, and at a pH-value which is generally from 3.5 to 6.5, the operating conditions substantially depending on the nature of the microorganism which is to be used in the subsequent stage. 35

Using the hydrolysates produced in this way, supplemented with nutrient elements, fermentation 40 is effected in the presence of organisms which are capable of producing cellulolytic enzymes. Such organisms are bacteria, preferably belonging to the genus *Clostridium* or fungi preferably belonging to the genera *Sporotrichum*, *Polyporus*, *Fusarium*, *Penicillium*, *Myrothecium* and *Trichoderma*. The fermentation operation which is carried out in anaerobic manner is performed for example with a bacterium of the genus *Clostridium* at a temperature which is generally between 25 and 40°C and at a 45 pH-value which is generally between 4 and 7.5. 45

The factors which have an influence on the composition of the mixtures produced are the strain used, the substrate and the fermentation conditions, that is to say, the pH-value, temperature, composition of the medium and in particular the nitrogen source.

The organisms used for the acetone/butanol fermentation operation generally belong to the genus 50 *Clostridium*. The species used have been described by the names *Clostridium saccharoacetobutylicum*, *Clostridium acetobutylicum*, *Clostridium saccharobutyl acetonicum*, and *Clostridium saccharoperbutylicum*. The type species is *Clostridium acetobutylicum*. 50

The organisms used for the butanol/isopropanol fermentation operation, which are close to those indicated above, also belong to the genus *Clostridium*. The species used have been described by the 55 names *Clostridium propylbutylicum*, and *Clostridium Viscifasciens*, but the type species used for this fermentation operation are *Clostridium butylicum* and *Clostridium beijerinckii* and *Clostridium toanum*. 55

Of the mixtures produced, use is advantageously made of mixtures containing for example about 75% by weight of n-butanol and 25% by weight of acetone or mixtures containing 60% by weight of n-butanol, 30% by weight of acetone and 10% by weight of ethanol.

Generally, using esters of types (a) and (b) defined hereinbefore as the fatty acid esters makes it possible to produce mixtures having good cold characteristics, but the proportion of alcohol constituent which can be employed is still relatively limited, for example restricted to values ranging up to about 25% by volume, in order for the cetane numbers of the mixtures produced still to be satisfactory.

5 In that case, recourse is therefore made to compositions which more particularly comprise: 5

- from 70 to 90% by volume of at least one fatty acid ester of types (a) and (b) defined hereinbefore, and
- from 30 to 10% by volume of alcohol constituent.

10 Of esters of type (a), consideration will be more particularly given to methyl oleate and methyl esters derived from colza oil, the "acid" part of which contains a reduced proportion of erucic acid, soya 10 oil, cotton oil and palm oil (in particular Dendé palm oil). Of esters of type (b), reference may be more particularly made to isopropyl myristate and methyl esters derived from copra oil or coconut oil (in particular babassu coconut oil).

15 The following Table sets out the main fatty acids which constitute the "acid part" of such 15 vegetable oils.

Oil of acid % by weight	COLZA	SÓYA	COTTON	PALM (Dendé)	COCONUT (babassu)	COPRA
SATURATED						
. Lauric	—	—	—	—	48	48
. Myristic	—	—	—	—	17.5	18
. Palmitic	—	6.5	21	42.5	9	10
. Stearic	—	—	—	—	—	—
UNSATURATED						
. Oleic	65	33.5	33	43	6	—
. Linoleic	20	52.5	43.5	9.5	—	—
. Linolenic	8	—	—	—	—	—

On the other hand, if the proportion of alcohol constituent in the mixture is to be increased to the maximum possible degree, for example up to 50% by volume, esters of type (c) defined hereinbefore will be advantageously employed. As the cold characteristics are then generally less good, the use of such 20 mixtures will require preheating thereof. Or again, they may be more particularly intended for hot 20 countries.

In that case, use may be made of compositions which more particularly comprise:

- from 50 to 90% by volume of at least one fatty acid ester of type (c) as defined hereinbefore and more specifically methyl or ethyl palmitate, methyl, ethyl or 2-ethylhexyl stearate, and methyl or ethyl 25 stearate/palmitate mixtures; and 25
- from 50 to 10% by volume of alcohol constituent.

It may be noted that using fatty acid esters in the combustible compositions according to the invention provides such compositions with additional proportion of alcohol in potential form resulting from the alkyloxy part of said esters, namely, depending on the circumstances involved, methanol, 30 ethanol, isopropanol or 2-ethylhexanol. 30

Thus, for example, a composition according to the invention which comprises 25% by volume of methanol and 75% by volume of methyl palmitate contains about 33% by weight of methanol, if account is taken of the potential methanol in the methyl palmitate. In the same way, a composition comprising 60% by volume of a mixture of ethyl stearate and palmitate and 40% by volume of absolute 35 ethanol contains about 49% by weight ethanol, if account is taken of the potential ethanol contained 35 in the ethyl stearate-palmitate mixture.

Among the advantages of using fatty acid esters in the combustible compositions according to the invention, such fatty acid esters make it possible to maintain the viscosity of the composition at a sufficiently high level, and thus to combat wear in the injection systems in diesel engines (pumps), such 40 wear generally being found when the engines are run on mixtures of gas oils and alcohols. 40

Moreover, some of the combustible compositions according to the invention, generally those which contain the most alcohol, may have a cetane number which is somewhat too low for satisfactory

use as base fuels for diesel engines. In that case, it is possible to increase the cetane number thereof by resorting to conventional additives such as alkyl nitrates (for example amyl, hexyl or octyl nitrate), which are then added in proportions of from about 0.1 to 5% by weight, so as to give a suitable cetane number, for example 40 or higher.

- 5 Finally, when the compositions according to the invention are used as fuels for diesel engines, it is possible to add thereto various conventional additives which are compatible with the fatty acid esters used. Thus, it may be recommended for the compositions to incorporate anti-oxidising additives. It is also possible to add thereto additives for improving cold characteristics, anti-smoke additives, etc.

- 10 The following Examples illustrate the invention and are in no way intended to limit the scope thereof to the particular embodiments described therein.

Preparation of methyl esters of colza oil which will be used in the combustible compositions according to the invention will first be described.

- 15 Taking a 10 litre glass Grignard reaction vessel provided with an agitator, a thermometer, a bottoms valve and an external heating means, there is introduced 5 kg of refined colza oil which has been previously dehydrated for 2 hours at 100°C, under an absolute pressure of from 6.5 to 7 millibars.

With the agitator means operative, the oil is heated to 55 to 60°C; thereafter, a solution comprising 876 g of absolute methanol and 9 g of metal sodium is incorporated in the oil, over a period of 5 minutes. The mixture is left to react for 1 hour, and the agitation is then stopped.

- 20 After 30 minutes settling time, the lower phase which essentially comprises glycerol (650 g) is removed by way of the bottoms valve. 620 cm³ of distilled water which has first been heated to 60°C is then added to the organic phase contained in the reaction vessel. After vigorous agitation for a period of 15 minutes, the mixture is left at rest for the same period of time. The aqueous washing phase which settles is removed as before. The washing operation is repeated twice with 320 cm³ of water.

- 25 The organic phase recovered is dried on anhydrous sodium sulphate, briefly filtered and then evaporated at 100°C under reduced pressure (6.5 to 7 millibars) for 1 hour, in order to remove therefrom the last traces of methanol.

Finally, 4750 g of the desired product is obtained, analysis thereof showing that the proportion of methyl esters therein is higher than 95% by weight.

- 30 Using a mode of operation identical to that described above, methyl esters of soya oil, cotton oil, palm oil, copra oil and babassu coconut oil were prepared.

The following Examples, which include some comparative data, illustrate but do not limit the present invention.

EXAMPLE 1

- 35 This Example describes the preparation of various combustible mixtures in accordance with the invention containing methanol as the alcohol constituent and various fatty acid esters.

The compositions of these mixtures, their cetane number and some of their cold characteristics are set out in Table I below.

TABLE I

Reference	Fatty acid ester	% Vol.	Methanol (% vol.)	Cetane number	Cloud point (°C)	Pour point (°C)
1 A (*)	methyl oleate 1	90	10	42.3	-12	-15
1 B	" "	80	20	37.4		
1 C (*)	methyl oleate 2	85	15	40.6	-4	-12
1 D	" "	80	20	37.6	+5	-42
1 E	co/za methyl esters	90	10	38.6	-7	-15
1 F	" "	80	20	36.1	0	-39
1 G	isopropyl myristate	80	20	41.1	0	-2
1 H	methyl palmitate	90	10	54.3	+28	+24
1 I	" "	85	15	53.2	+26	+21
1 J	" "	75	25	41.0	+24	+21
1 K	" "	65	35	32.0	+21	+18
1 L	2-ethylhexyl stearate	85	15	53.9	+44	0
1 M	coconut methyl esters	90	10	49	-	-
1 N	" " "	80	20	45.1	-	-
1 P	palm methyl esters	90	10	46	-	-
1 Q	" " "	80	20	41	-	-
1 R	cotton methyl esters	85	15	40	-	-

(*) Two methyl oleates from different sources were used.

The characteristics of the resulting mixtures show in particular that it is possible to use up to about 15% by volume of methanol mixed with methyl oleates, while maintaining good cetane numbers and good cold characteristics. On the other hand, with a fatty acid ester such as methyl palmitate, it is possible to use methanol contents which range up to about 25% by volume: the cetane numbers are excellent but the cloud point and the pour point are markedly worse (the combustible mixture has to be preheated).

For mixtures whose cetane number is unsatisfactory (below about 40), the value of the cetane number has been raised to more than 40 by the addition of a cetane number improving additive, amyl nitrate, in a proportion of from 0.5 to 2%, according to the case in question. The same will arise in connection with Examples 2, 3 and 5.

EXAMPLE 2

This Example describes the use of absolute ethanol mixed with various fatty acid esters.

The composition of the mixtures, their cetane number, their cloud point and their pour point are set in Table II below.

TABLE II

Reference	Fatty acid ester	% Vol.	Ethanol (% vol.)	Cetane number	Cloud point (°C)	Pour point (°C)
2 A	methyl oleate 1	90	10	44.3	-11	-14
2 B	" "	80	20	38.4	-12	-12
2 C	" "	70	30	35.7	-12	-15
2 D	methyl oleate 2	70	30	36.5	-9	-12
2 E	colza methyl esters	90	10	40.4	-7	-18
2 F	" "	80	20	36.3	-7	-18
2 G	copra methyl esters	80	20	40.4	-1	-9
2 H	" "	70	30	36.1	-3	-9
2 I	methyl palmitate	80	20	49.9	+24	+21
2 J	" "	70	30	38.1	+27	+21
2 K	2-ethylhexyl stearate	70	30	39.6	+5	+3
2 L	ethyl { palmitate stearate	60	40	38.5	+21	+21
2 M	coconut methyl esters	75	25	40.2	-	-
2 N	palm methyl esters	80	20	41.0	-	-
2 P	soya methyl esters	90	10	41.0	-	-
2 Q	cotton methyl esters	85	15	41.5	-	-

EXAMPLE 3

This Example uses the azeotrope of ethanol and water, containing about 95% by weight of ethanol and about 5% of water. Mixtures are made, comprising varying proportions, with various fatty acid esters, as set out in Table III below.

- 5 The mixtures which are formed in this way are stable (no separation of the constituents of the mixture), in spite of the presence of 5% by weight of water in the ethanol. 5

EXAMPLE 4 (Comparative)

- 10 The attempt was made to prepare similar mixtures by using 90% ethanol as the alcohol constituent. It was not possible to produce stable mixtures with the various fatty acid esters tried, even with relatively low proportions (10% by volume) of 90% ethanol. 10

EXAMPLE 5

This Example describes mixtures in which the alcohol constituent itself comprises a mixture of 75% by weight of n-butanol and 25% by weight of acetone (referred to as MBA : mixture of butanol and acetone).

- 15 The composition of the combustible mixtures, their cetane number, their cloud point and their pour point are set out in Table IV below. 15

EXAMPLE 6 : Tests on a diesel engine

Some of the compositions according to the invention were tested on an agricultural tractor diesel engine (speed of 2400 r.p.m.), for 50 hours for each composition.

- 20 The compositions tested were: 20
- mixtures designated 1 C and 1 G in Example 1;
 - mixtures designated 2 G and 2 K in Example 2;
 - the mixture designated 3 B in Example 3; and
 - mixtures designated 5 D and 5 E in Example 5.
- 25 These tests did not result in any trouble or breakdown in operation of the engine. No deposits at the injectors were found. Moreover, it was observed that the power output of the engine was maintained in the normal fashion, 25

TABLE III

Reference	Fatty acid ester	% Vol.	95% ethanol % vol.	Cetane number	Cloud point (°C)	Pour point (°C)
3 A	methyl oleate	80	10	44.9	+ 6	-15
3 B	" "	80	20	39.0	+10	-15
3 C	" "	70	30	34.1	+ 6	-18
3 D	isopropyl myristate	70	30	36.0	+ 0	0
3 E	copra methyl esters	70	30	34.3	- 5	- 6
3 F	ethyl { palmitate stearate	70	30	39.0	-26	+21
3 G	coconut methyl esters	80	20	42.0	-	-
3 H	palm methyl esters	85	15	40.5	-	-
3 I	cotton methyl esters	80	20	39.8	-	-

TABLE IV

Reference	Fatty acid ester	% vol.	MEA % vol.	Cetane number	Cloud point (°C)	Pour point (°C)
5 A	methyl oleate	80	10	44.9	-14	-15
5 B	" "	80	20	39.9	-15	-18
5 C	" "	70	30	37.6	-15	-18
5 D	ethyl { palmitate stearate	60	40	39.5	+20	+15
5 E	coconut methyl esters	70	30	43	-	-

CLAIMS

1. A combustible composition comprising a stable mixture of from 50 to 90% by volume of at least one C_{1-8} alkyl ester of a C_{12-22} fatty acid, and from 50 to 10% by volume of at least one alcoholic constituent comprising at least one primary, secondary or tertiary aliphatic monohydric C_{1-5} alcohol. 5
2. A composition according to Claim 1 in which the alcoholic constituent is methanol.
3. A composition according to Claim 1 in which the alcoholic constituent is absolute ethanol.
4. A composition according to Claim 1 in which the alcoholic constituent is an ethanol-water azeotrope containing about 95% by weight of ethanol.
5. A composition according to Claim 1 in which the alcoholic constituent comprises a mixture of about 75% by weight of *n*-butanol and about 25% by weight of acetone. 10
6. A composition according to Claim 1 in which the alcoholic constituent comprises a mixture of about 60% by weight of *n*-butanol, about 30% by weight of acetone and about 10% by weight of ethanol.
7. A composition according to any one of Claims 1 to 6 comprising from 70 to 90% by volume of at least one fatty acid ester in which the acid residue has an unsaturated C_{16-22} chain, and from 30 to 10% by volume of the alcoholic constituent. 15
8. A composition according to Claim 7 in which the fatty acid ester is methyl oleate or a mixture of methyl esters derived from colza, soya, cotton or palm oil.
9. A composition according to any one of Claims 1 to 6 comprising from 70 to 90% by volume of at least one fatty acid ester in which the acid residue has an unsaturated C_{12-14} chain, and from 30 to 10% by volume of the alcoholic constituent. 20
10. A composition according to Claim 9 in which the fatty acid ester is isopropyl myristate or a mixture of methyl esters derived from copra oil or coconut oil.
11. A composition according to any one of Claims 1 to 6 comprising from 50 to 90% by volume of at least one fatty acid ester in which the acid residue has a saturated $C_{16 \times 18}$ chain, and from 50 to 10% by 25 volume of the alcoholic constituent.
12. A composition according to Claim 11 in which the fatty acid ester is methyl palmitate, methyl stearate, ethyl stearate, 2-ethylhexyl stearate, a mixture of methyl stearate and methyl palmitate, or a mixture of ethyl stearate and ethyl palmitate.
13. A composition according to any one of Claims 1 to 12 having a cetane number of at least 40. 30
14. A composition according to any one of Claims 1 to 12 that further comprises a proportion of cetane-number-improving additive(s) sufficient to give a cetane number of at least 40.
15. A composition according to any one of Claims 1 to 14 that further contains a suitable proportion of at least one anti-oxidant.
16. A composition according to Claim 1 substantially as herein-before described in any one of 35 Examples 1, 2, 3 and 5.
17. A composition according to any one of Claims 1 to 16 for use as fuel for a diesel engine.